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Origin of the enhanced space-charge-limited current in poly(*p*-phenylene vinylene)

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It is demonstrated that the enhancement of the space-charge-limited (SCL) hole current of poly(*p*-phenylene vinylene) (PPV) derivatives at high bias at room temperature is due to the carrier density dependence of the hole mobility. Contrary to numerous reports the dependence of the mobility on the electric field is only observed at low temperatures. Analysis of the hole transport without taking into account the charge carrier density dependence of the mobility leads to an incorrect charge carrier and electric field distributions in organic light-emitting diodes.

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Since the discovery of electroluminescence in poly(*p*-phenylene vinylene) (PPV), light-emitting diodes (LED's) made from π-conjugated polymers have been studied extensively.[1] It has been recognized that the charge transport properties are of great importance for the operation and the efficiency of polymer based LED's. The current through polymer LED's based on poly[2-methoxy-5-(3′, 7′-dimethyloctyloxy)-*p*-phenylene vinylene] (OC_1C_{10}-PPV) is space-charge limited (SCL) and governed by a constant hole mobility (μ_h) of 5×10^{-11} $m^2/V\,s$ at low bias voltages at room temperature.[2] At high bias voltages the field and temperature dependence of the SCL current have been described with an empirical law for the hole mobility:[3]

$$\mu_h(E,T) = \mu_h(0,T)\exp[\gamma(T)\sqrt{E}], \tag{1}$$

with $\mu_h(0,T)$ the hole mobility at zero field and $\gamma(T)$ the field activation factor, which reflects the lowering of the hopping barriers in the direction of the applied electric field. Introduced to explain the charge transport in OC_1C_{10}-PPV,[3] the concept of a SCL current and a field- and temperature-dependent mobility has been extensively applied to transport measurements on organic semiconductors. For instance, it has been used to analyze the charge carrier mobility of various PPV derivatives,[4,5] the current and transient transport in various PPV and polyfluorene derivatives,[6,7] as well as the electron transport in diodes based on small molecules of tris(8-hydroxyquinolato)aluminum.[8] Furthermore, the field-dependent mobility [Eq. (1)] has also been incorporated in numerical simulations to model the current-voltage characteristics and the transients of PPV-based LED's.[9–11]

In a recent study the dependence of the hole mobility μ_h on the carrier density in OC_1C_{10}-PPV has been investigated by a combined study on polymeric diodes and field-effect transistors.[12] It has been demonstrated that the hole mobility of OC_1C_{10}-PPV is constant for charge carrier densities typically $<10^{22}$ m^{-3} and increases with a power law with density for carrier densities $>10^{22}$ m^{-3}. In the analysis of charge transport properties of polymeric SCL devices such dependence has not yet been taken into account. In a space-charge-limited device an increase of the applied bias gives rise to a simultaneous increase of the electric field and charge carrier density. Consequently, the contributions of the charge carrier density and the electric field to the mobility cannot be disentangled from a SCL current. For the understanding of the charge transport in polymeric devices it is of fundamental importance to know whether the current is governed by the field and/or the carrier density dependence of the mobility. In this work we demonstrate that the enhancement of the current density in SCL diodes is dominated by the carrier density dependence of the hole mobility at room temperature and, in contrast to what has been assumed so far,[3–11] not by its field dependence. Analysis of the transport data without taking the density dependence of μ_h into account leads to an incorrect charge carrier and field distribution in organic SCL diodes.

The devices used in this study consist of OC_1C_{10}-PPV as the active semiconductor in a hole-only diode and in a field-effect transistor (FET). The field-effect structure has been described previously.[12] In the hole-only diode OC_1C_{10}-PPV is sandwiched between an indium tin oxide (ITO) anode and a gold (Au) cathode. In Fig. 1 the current density-voltage ($J-V$) measurements for hole-only diodes are shown for various temperatures. At room temperature the SCL current increases quadratically with the applied field up to an applied bias of 1 V. In this bias range the hole mobility is indepen-

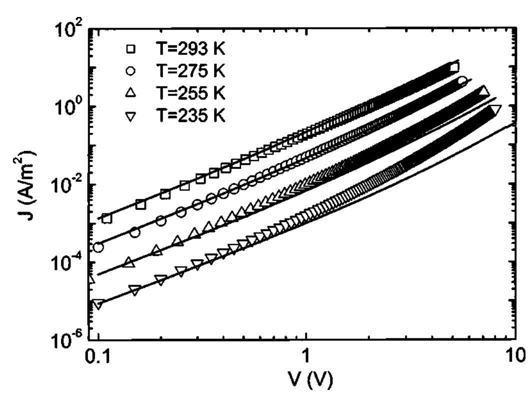

FIG. 1. Temperature-dependent current density vs voltage characteristics of OC_1C_{10}-PPV hole-only diode. The solid lines represent the prediction from the SCL model including the density-dependent mobility [Eq. (2)].

dent on both electric field and charge carrier density and amounts to 5×10^{-11} m^2/V s. However, at high bias the current density increases more than quadratically with the applied bias. This enhancement is the more pronounced the lower the temperature.

Recently, the dependence of the mobility on the charge carrier density has been obtained from the transfer characteristics of OC_1C_{10}-PPV based field-effect transistors (FET's).[12] The experimental field-effect mobility μ_{FET} is directly calculated by differentiating the channel current I_d with respect to the gate voltage V_g. The field-effect mobility increases superlinearly with the charge carrier density. The dependence has been quantitatively interpreted using a hopping percolation model in an exponential density of states (DOS),[13] which is a good approximation of the tail states of the Gaussian DOS.[12] Unification of the diode and field-effect measurements shows that the dependence of the hole mobility on charge carrier density is given by

$$\mu_h(p,T) = \mu_h(0,T) + \frac{\sigma_0}{e}\left(\frac{\left(\frac{T_0}{T}\right)^4 \sin\left(\pi\frac{T}{T_0}\right)}{(2\alpha)^3 B_c}\right)^{T_0/T} p^{T_0/T-1}, \tag{2}$$

where $\mu_h(0,T)$ is the hole mobility at low densities obtained from the quadratic SCL current, σ_0 is a prefactor for the conductivity, α^{-1} is the effective overlap parameter between localized states, T_0 is a measure of the width of the exponential density of states, and B_c is the critical number for the onset of percolation. The parameters σ_0, α^{-1}, and T_0 are obtained from the temperature dependence of the transfer characteristics of the FET. These transfer characteristics are consistently described by a single set of values, namely, $T_0=540$ K, $\sigma_0=3.1\times10^7$ S/m, $\alpha^{-1}=0.14$ nm, and $B_c=2.8$.[12] It should be noted that this unification is only possible for highly disordered polymers as OC_1C_{10}-PPV, in which the charge transport is isotropic.[12] For more ordered PPV derivatives with higher field-effect mobilities the transport is anisotropic and unification is not possible.[14] In Fig. 2(a) the experimental mobility (symbols) and the dependence of the mobility on charge carrier density calculated using Eq. (2) (solid lines) are presented for various temperatures and carrier densities in the range of 3×10^{20} to 3×10^{25} m^{-3} for OC_1C_{10}-PPV. A good agreement between experimental and calculated mobilities is obtained. This experimentally determined mobility dependence on carrier density now enables us to disentangle the contributions of the electric field and the carrier density to the enhancement of the SCL current at high bias.

As a first step the SCL current is calculated using only the density-dependent mobility as given by Eq. (2). In these calculations any field dependence of the mobility is disregarded. It should be noted that the density dependence of the mobility as given by Eq. (2) does not contain a fit parameter; the mobility at low density directly follows from the quadratic part of the $J-V$ characteristics, whereas the power-law dependence at high carrier densities is independently measured in the FET. The SCL current is now calculated by combining Eq. (2) with

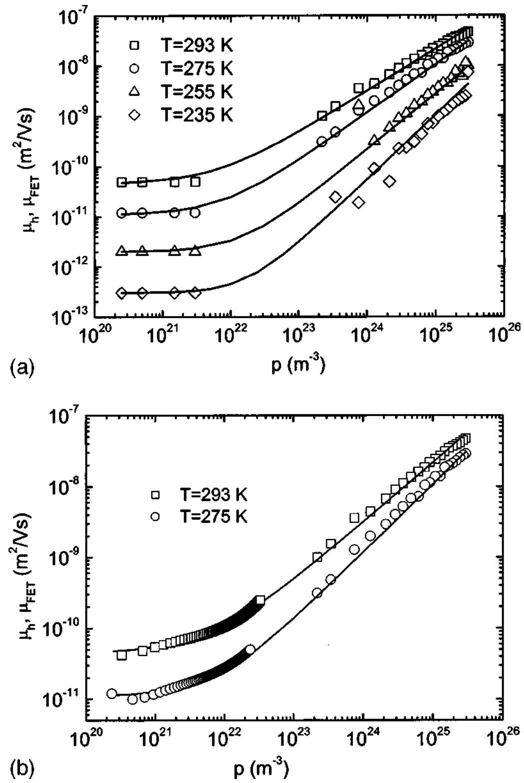

FIG. 2. (a), (b) Temperature-dependent mobility $\mu_h(p,T)$ vs hole density for OC_1C_{10}-PPV. The solid lines are the calculated $\mu_h(p,T)$ using Eq. (2) with the parameters mentioned in the text.

$$J = p(x)e\mu_h[p(x)]E(x), \tag{3}$$

$$\frac{\varepsilon_0\varepsilon_r}{e}\frac{dE(x)}{dx} = p(x), \tag{4}$$

with $p(x)$ the density of holes at position x. By numerically solving Eqs. (2)–(4) the $J-V$ characteristics are obtained, as shown in Fig. 1 by the solid lines. Figure 1 shows that at $T=275$ K and $T=293$ K the calculated SCL current density for OC_1C_{10}-PPV at high fields using Eqs. (2)–(4) is in good agreement with the experimental current densities. Surprisingly, a possible field dependence of μ_h, which has been used as an explanation for the SCL current enhancement at high bias so far,[3–11] is not required to describe the experimental $J-V$ characteristics. Therefore, the field enhancement of the mobility at room temperature is only a minor effect. As an upper limit we estimated that $\gamma(T)$ at room temperature is at least more than an order of magnitude lower than previously reported values.[3] Furthermore, from Fig. 1 it appears that at temperatures lower than $T=275$ K the carrier density dependence of the mobility alone does not explain the observed increase of the SCLC. Apparently, at low temperatures the field dependence of the mobility becomes important. At present, there is no theoretical model available describing the field activation at both low and high carrier densities. Consequently, at low temperatures where both field and density dependence play a role the $J-V$ characteristics cannot yet be related to microscopic transport parameters as a density of states or an average transport site spacing.

The experimental mobility versus density plot of Fig. 2(a) exhibits a gap at the 10^{22}–10^{23} m^{-3} density range. This density range is not accessible by FET measurements since it would require very small gate voltages, resulting in channel currents below the measurement accuracy. The LED data at voltages higher than 1 V (carrier densities $>3\times10^{21}$ m^{-3}) were not used since the carrier density dependence of μ_h cannot be discriminated from the field dependence of μ_h. However, the observed dominance of the density dependence of the mobility on the SCL current at $T>255$ K now enables us to determine the mobility-density relation directly from the $J-V$ characteristics over the full voltage range. By comparison with numerical simulations, we obtained that the SCL current, with a density dependent mobility according to Eq. (2) through a device with thickness L, can be accurately approximated by

$$J = 0.8ep_{\mathrm{av}}\mu_h(p_{\mathrm{av}})E_{\mathrm{av}}, \tag{5}$$

with $E_{\mathrm{av}}=V/L$, p_{av} the average density in the device given by $p_{\mathrm{av}}=1.5(\varepsilon_0\varepsilon_r V/eL^2)$,[15] and $\mu_h(p_{\mathrm{av}})$ the mobility at density p_{av}. For an experimental $J-V$ characteristic E_{av} and p_{av} can be directly calculated for any applied voltage V and from the corresponding J the mobility μ_{av} follows directly from Eq. (5). We tested this approximation by using the numerically simulated $J-V$ characteristics, with $\mu_h(p,T)$ from Eq. (2), as input for the above-mentioned procedure. The resulting $\mu_{\mathrm{av}}(p_{\mathrm{av}})$ relation followed the analytical $\mu_h(p,T)$ relation [Eq. (2)] within a few percent. After this confirmation, the procedure has been used to extract the mobility/density relation directly from the experimental $J-V$ curves (Fig. 1) at $T=275$ K and 293 K. The result is shown in Fig. 2(b) together with the transistor data. The experimental SCLC and FET mobilities adjust very well and now nearly cover the whole density range. As a result the combination of $J-V$ and field-effect measurements provides a consistent description of the mobility-density relation in OC_1C_{10}-PPV, and is indeed well described by Eq. (2) as previously assumed. In fact, since the onset of the power law is already clearly visible from the SCLC measurement, the complete current transport in a FET can be predicted from the hole-only diode measurements. The same analysis has been applied to other disordered polymers and similar consistent mobility-density dependencies have been found.

The fundamental question whether the increase of the mobility in a SCL device is dominated by either the carrier density or the electric field is relevant for the operation of light-emitting diodes. In Fig. 3 the distribution of the electric field $E(x)$ as a function of distance x from the ITO injecting anode is plotted in a single carrier SCL diode. For a constant mobility the electric field varies with position as $E(x)=(2Jx/\varepsilon_0\varepsilon_r\mu_h)^{1/2}$ (dotted line), and the hole concentration with $p\propto x^{-1/2}$. For a mobility that only depends on the electric field [Eq. (1)] the charge carriers close to the injection contact will experience a low field. The charge carriers close to the Au noninjecting cathode on the other hand will experience a high field with resulting field-enhanced mobility.

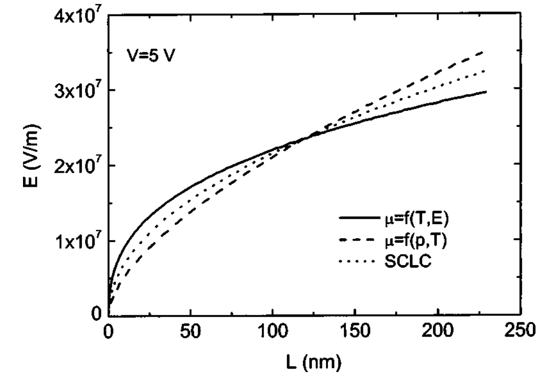

FIG. 3. Calculated distribution of the electric field $E(x)$ in OC_1C_{10}-PPV diode biased at 5 V at $T=295$ K: the distribution $E(x)=(2Jx/\varepsilon_0\varepsilon_r\mu_h)^{1/2}$ for a constant mobility (dotted line); the distribution for a field-dependent mobility [Eq. (1)] using $\gamma=5\times10^{-4}$ $(m/V)^{1/2}$ (solid line); the distribution for a charge carrier density dependent mobility [Eq. (2)] (dashed line).

Since the current through the device is position independent the field close to the injecting contact will be increased, whereas the field at the collecting contact will be decreased, as shown in Fig. 3 (solid line). However, for a mobility that is dominated by the carrier density the mobility will be large close to the injecting contact, where the charge carrier density is largest, and low at the collecting contact. Consequently, the field will be enhanced at the collecting contact and reduced at the injecting contact, in contrast to the field dependent case (Fig. 3, dashed line). Figure 3 shows that the electric field distribution in a polymeric SCL diode is strongly dependent on the microscopic origin for the mobility enhancement. In the present device models describing the electrical characteristics of polymer LED's only a field-dependent mobility has been incorporated.[9–11] The dominance of the carrier density dependent mobility at room temperature will clearly modify the reported field- and carrier distributions. At low temperatures the distribution of the electric field become closer to earlier reported model calculations, because the field dependence becomes more important. This is due to the fact that at low temperatures the activated hops between neighboring sites are strongly suppressed and limit the charge transport. The application of an electric field leads to a reduction of these dominant barriers for the charge transport in the field direction, resulting in a strong field dependence.

In conclusion, we have demonstrated that the space-charge-limited current in devices based on the conjugated polymer OC_1C_{10}-PPV is governed by the dependence of the hole mobility on electric field and charge carrier density. At room temperature the charge carrier density dependence of the mobility is dominant, in contrast to earlier reported results, while at low temperatures the field dependence of the mobility must be considered. Omission of the density dependence leads to an underestimation of the field at the collecting contact.

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